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Study of the heats of dilution

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**A STUDY OF THE HEATS OF DILUTION OF
SOLUTIONS OF BARIUM CHLORIDE AND
BARIUM-SODIUM CHLORIDE MIXTURE**

BY

RAPLH FRED SCHNEIDER

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

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1919

1918, 1919

1. The first part of the paper is devoted to a general discussion of the problem of the existence of solutions of the system of equations (1) and (2) under the conditions (3) and (4). It is shown that the system has a solution if and only if the conditions (5) and (6) are satisfied.

2. THE CASE OF A SINGLE EQUATION

In the case of a single equation the system (1) and (2) reduces to the equation (7). It is shown that the equation (7) has a solution if and only if the conditions (8) and (9) are satisfied. The case of a single equation is considered in detail in the next section.

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3. THE CASE OF A SYSTEM OF EQUATIONS

In the case of a system of equations the system (1) and (2) reduces to the system (10).

It is shown that the system (10) has a solution if and only if the conditions (11) and (12) are satisfied.

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Ralph F. Schneider

ENTITLED..... A STUDY OF THE HEATS OF DILUTION OF SOLUTIONS OF

BARIUM CHLORIDE AND BARIUM-SODIUM CHLORIDE MIXTURE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Ralph F. Schneider



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CONTENTS.

	page.
INTRODUCTION	1
MATERIALS	2
APPARATUS	2
METHOD	13
EXPERIMENTAL DATA	15
DISCUSSION	23
SUMMARY	34
BIBLIOGRAPHY	35

INTRODUCTION.

PURPOSE OF THE INVESTIGATION. In connection with some work done in this laboratory on the heats of dilution of mixed salt solutions of strontium chloride with certain of the alkali chlorides ⁽¹⁾ it was thought to be of interest to measure the reversible molal heats of dilution of solutions of barium chloride and of equivalent mixtures of barium and sodium chlorides, and thus ascertain whether the results obtained in the case of strontium were unique. The behavior of the barium chloride solution itself would be of interest inasmuch as the strontium chloride in solution behaves differently from the two uni-univalent salts, sodium chloride and potassium chloride. This is due, perhaps, to the bivalent strontium and to its ionization in partial stages to intermediate ions such as the SrCl^- ion. In concentrated solutions this intermediate ion is perhaps the only simple ionic form of the strontium.

MATERIALS.

The sodium and barium chlorides were of various brands all labeled C.P. Previous work⁽¹⁾ along this same line as well as this work has shown that the heat effects in solutions as concentrated as 0.2 weight normal are so small as to be hardly measurable. Thus, inasmuch as small amounts of impurities have no effect on the results in this work, it was considered unnecessary to purify them further.

APPARATUS.

THE CALORIMETER used was a very slight modification of the adiabatic calorimeter of MacInnes and Braham.⁽²⁾ The calorimeter proper is outlined in cross section in Fig. 2 and a view from the top is shown in Fig. 1. These figures, together with Figs. 3, 4, and 5, are taken by kind permission of Dr. MacInnes from MacInnes and Braham's article on the instrument. The calorimeter vessel A-A, a ten liter vessel made of heavy copper and nickle plated, is separated from a similar surrounding vessel B-B by a 6 mm. air space. The separation is effected by a rubber gasket a, and a supporting ring of hard rubber, o. The seams of both vessels are brazed. B-B is supported on brass legs, b, that fit into holes in a wooden false bottom in a larger vessel C. "The vessel B-B carries the cover M-M of 3 mm. brass which can be clamped on the 2 cm. flange of B-B. A rubber gasket, e-e, is interposed between the cover and the flange. Screwed into the cover

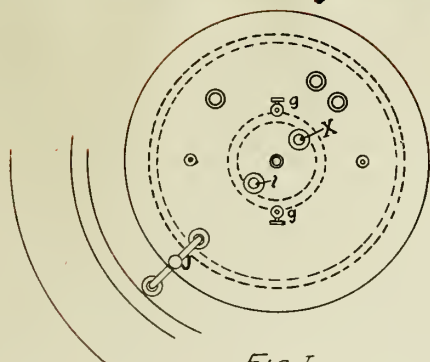


FIG. 1

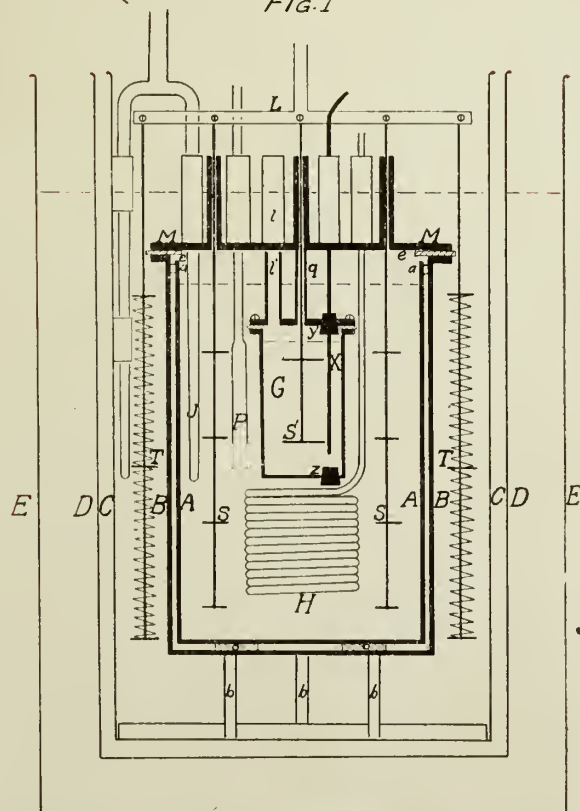


FIG. 2

are a number of tubes, each two inches long, through which pass the platinum resistance thermometer P, the leads from the heater, H, the arms from the stirrers, S-S, and S', the wire supports g-g, of the dilution cup, C, one leg of the thermojunction, J, and the rod, X. The tube, l, is for the purpose of filling the dilution cup.

"The sides of the dilution cup, C, are made of thin sheet copper fastened to a brass ring at the top and to a sheet brass bottom. A brass cover 3 mm. thick carries the tubes l' and q. This cover makes a water-tight connection with the ring at the top of the cup by means of the rubber gasket and screws as shown. The tube l' fits under l, and is used for filling the cup. The stirrer S' passes through the tube q. In a vertical line under a tube in the calorimeter cover M-M two holes, y and z, are bored in the cover and bottom of the dilution cup. The hole y is closed by a rubber stopper fastened to a brass rod, X; the holes y and z can be opened in turn. The cup is held in place by means of wires fastened into tubes in the cover M-M."

The stirrer S-S consists of four brass disks with holes punched in them at intervals.

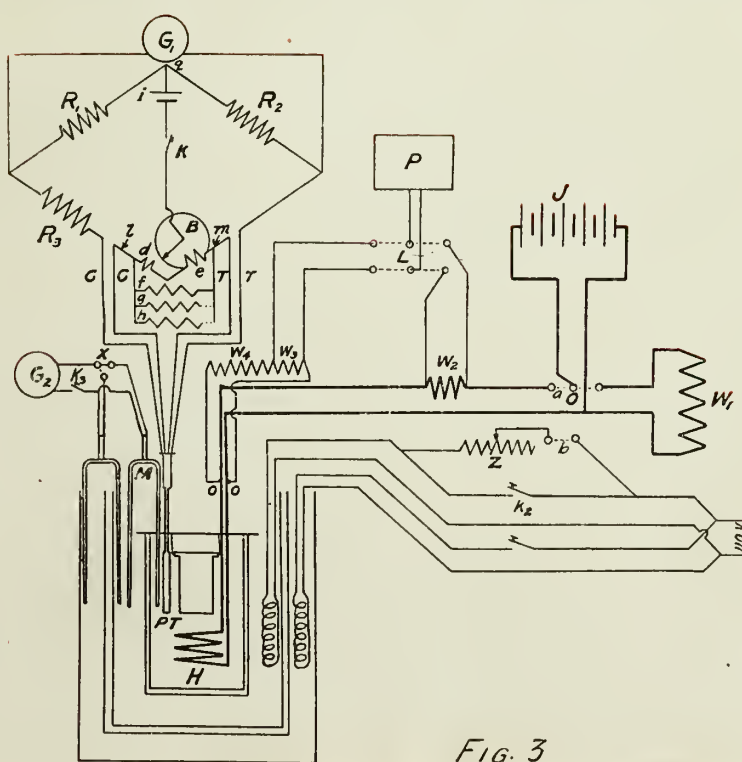
The space between the vessels B and C is filled with water. This space will be referred to as the "surroundings". In this space is placed a stirrer T-T, consisting of three galvanized iron disks each containing eight holes. "This stirrer carries four coils each containing eight meters of number 18 nichrome wire. The coils pass through the stirrer disks on wooden insula-

tors and are arranged diagonally to the direction of motion of the stirrer. These coils are connected in series through a key to a source of 110 volt alternating current. "Thus the temperature of the surroundings can be raised at any time.

"The stirrers S-S, S' and T-T are all connected to the yoke L, which is given an up and down motion of 5 cm. sixty times a minute by means of a crank operated through a system of pulleys by a one sixth horse power motor. This method of stirring has been demonstrated to be extremely efficient.

"The vessels C, D, and E are of heavy galvanized iron. Vessel D is separated from vessel C by an air space." The space between vessels D and E is filled with water. This in itself gives a rough regulation of the radiation from the "surroundings". This regulation may be made easier by regulating the temperature of the water in this space by means of a stirrer and a heating coil much the same as the system in the space between vessels B and C.

THE PLATINUM RESISTANCE THERMOMETER was one designed by Dickinson and Mueller⁽³⁾ and made by Leeds and Northrup. The resistance of the thermometer was measured by means of a Wheatstone bridge designed also by Dickinson and Mueller and manufactured by Leeds and Northrup. The upper right hand corner of Fig. 5 shows a diagram of the bridge and connections. R_3 is an adjustable resistance of 100 ohms, the lowest coils being 0.01 ohm. In this arm of the bridge the compensative leads, c-c, of the thermometer are placed in series. The main leads, T-T, of the thermometer are connected in the remaining arm. R_1 and R_2 repre-



sent the ratio coils. Those used were 100 ohms each. The bridge wire, B, shunted by a resistance, e, is also placed in the arm with the main thermometer leads. " 'd' is a resistance equal to that of the shunted bridge wire, 0.55 ohms. The shunts f, g, and h are so arranged that the resistance between the points l and m can be adjusted to 0.11, 0.22, or 0.55 ohm, equal respectively to the increase in resistance when the temperature of a 25 ohm thermometer is increased roughly 1.1° , 2.2° , or 5.5° . The shunt which gives a change in resistance corresponding to 1.1° is the one which was used. Since each turn of the bridge wire is graduated in 200 divisions which can be readily estimated to fifths, temperature changes corresponding to 0.0001° can be read with ease.

"A dry cell, i, is connected through a key, k, between the junction of the ratio coils, q, and the sliding contact on the bridge wire, d."

The galvanometer, G, is a Leeds and Northrup "high sensitivity" galvanometer with a sensitivity of about 2 mm. per microvolt at a scale distance of one meter. Its resistance is 13.5 ohms.

"A DIFFERENTIAL THERMOMETER, M (Fig. 3), consisting of a set of sixteen copper-constantin thermojunctions is employed to measure the constant temperature difference maintained between the calorimeter and 'surroundings' during a determination." The instrument is connected in series with a galvanometer in such a way that a temperature difference of 0.15° gives a deflection of about 20 mm. at a scale distance of one meter. It is connected

through a key, k_3 , so that the circuit may be opened at any time and any shift from the zero position corrected. During a part of this work another set of thermojunctions, less sensitive, was placed between the 'surroundings' and the outer bath. By means of a double switch, X, the same galvanometer, G_2 , could be used with either set of junctions.

THE HEATERS AND CONNECTIONS are shown on the right side of Fig. 3. The source of heat for the calorimeter coil, J, consisted of a storage battery arranged to deliver 10 volts. By means of the switch at o the current can be made to pass through the heater H, or through a polarizing resistance W_1 , equal to the resistance of the heater. A preliminary polarization of the cells by passing the current through W_1 insures a steadier current when they are connected to the heater.

W_2 is an accurately known resistance of 0.6419 ohm in series with the heater. It is designed to carry up to three amperes without changing its resistance. From the terminals of W_2 leads are run to the double throw switch L, and thence to the potentiometer, P. From the potentiometer reading and the value of W_2 the current passing through the heater can be calculated.

"The resistances W_3 and W_4 are shunted across the terminals O-O of the heater H. W_4 is 10,000 ohms and W_3 is adjusted so that the voltage at its terminals is approximately equal to the potential drop through W_2 ." The potential drop across W_3 can also be read on the potentiometer P by adjustment of the switch L. From this value and a knowledge of the values of W_3 and W_4 the E.M.F. drop through the heater can be calculated. The potentiometer

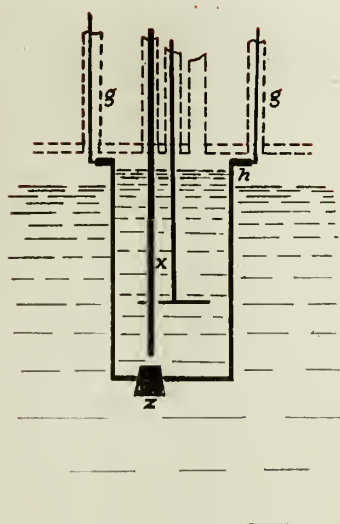


FIG. 4

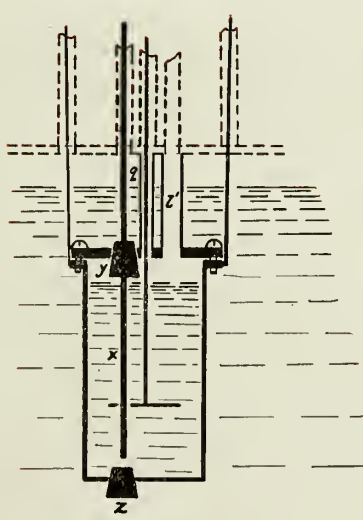


FIG. 5

is equipped with a Leeds and Northrup portable galvanometer of one megohm sensitivity. It is adjusted by means of a Weston standard cell. The time during which current is passed into the heater is measured by means of a stop watch which has been repeatedly compared with an accurate clock.

The simultaneous introduction of heat into the calorimeter and "surroundings" is brought about by the switch at o. The connectors a and b work together so that when the current from the storage battery is shifted from the polarizing resistance to the heater, the alternating current from a 110 volt source is at the same time sent through the coils in the "surroundings". The rheostat, z, is in series with the alternating current, and the sliding contact is so placed as to keep the difference in temperature between the calorimeter and the "surroundings" constant, leaving the operator free to read the potentiometer. A key, k_2 , is arranged so as to be able to "short" the full strength of the alternating current through the coils of the "surroundings". The external bath is provided with a similar arrangement not shown in the diagram.

Fig. 5 shows the design of the dilution cup. With this design, which is an improvement over that shown in Fig. 4 - one of the previous designs - the "dilution of water with water is unaccompanied by any heat effect." Holes y and z, in a vertical line under a tube in the calorimeter cover, are closed with rubber stoppers, one of which is attached to the rod, X. "The entire cup is submerged in the liquid in the calorimeter. To operate, the rod X is pushed down, carrying the stopper in the hole

y with it. The solution rushes into the free space in the cup. The stopper in z is then displaced and the circulation through the cup soon causes thorough mixing.

In making a calorimetric determination, a weighed quantity of a salt solution of a known concentration is introduced into the calorimeter vessel. The apparatus is then assembled and a weighed amount of water introduced through the tubes l and l' (Fig. 2) into the dilution cup. The "surroundings" are filled with water at a temperature slightly lower than that of the solution in the calorimeter. The differential thermometer and platinum resistance thermometer are inserted and the stirring commenced. The "surroundings" are then slowly heated by closing key k_2 intermittently until the difference in temperature between them and the calorimeter liquid is about 0.15° as shown by the throw of galvanometer G_2 . After one to three hours, giving time for complete uniformity of temperature in the dilution water and the solution, readings of the temperature of the calorimeter are taken until they are constant to 0.0001° for from five to ten minutes.

From here on the procedure varies according to whether the heat of dilution, as determined by a preliminary trial, is positive or negative. If it is positive, the solution is directly diluted, and after allowing sufficient time for mixing, constant temperature readings are again obtained. Next, current is passed through the heater for a known length of time, and finally the temperature is again read when constant. The procedure in the case of negative heats where these are comparatively large

is to introduce heat into the solution by means of the electric current at a slightly more rapid rate than it is taken up in dilution. Then, after finishing the run as described above, one can calculate the number of calories corresponding to the electrical energy introduced, and the actual number of calories corresponding to the increase in temperature. The difference would be the number of calories due to the heat of dilution. By this procedure the heat capacity of the calorimeter is measured as a part of every determination, and thus inaccuracies due to calculations from questionable data on specific heats of solutions, water equivalent of the calorimeter, slightly varying conditions of experiments, uncertainties arising from the calibration of the thermometer, etc., are eliminated. Thus by a simple proportion the heat of dilution can be obtained at once. For if H_D is the heat due to dilution, expressed in joules, then

$$H_D : EIT = R_D : R_E$$

where E is electromotive force, I the current, and T the time in seconds during which the current is passed through the calorimeter. R_D and R_E are the changes in temperature, in resistance units, due respectively to the dilution and to the electrical heating.

$$\text{Or - } H_D \text{ (in calories)} : \frac{EIT}{J} = R_D : R_E$$

where J represents Joule's equivalent, 4.184 joules per calorie.

Since the relation between the change in resistance and the temperature change is not linear, any large values of R_D or R_E would have to be corrected by means of the relation,

$$\Delta t = \frac{100}{(R_{100} - R_0) \left(1 + \frac{d'}{100} - \frac{2d'T}{100^2} \right)} \Delta R$$

in which R_{100} is the resistance of the thermometer in steam at 760 mm. Hg. pressure, R_0 is its resistance in melting ice, and d' is an empirical constant. MacInnes and Braham determined R_{100} and R_0 for the thermometers employed, and used for d' the value 1.47, recommended by the Bureau of Standards. They found, however, that with the values of R_D and R_E of the magnitude met with in their work, which were even greater than those met with in this investigation, the correction was too small to affect their numerical results in any way; so that if $\Delta R = 0.02395$, then $\Delta t = 0.2395$, just ten times the numerical value of ΔR .

METHOD.

The salt solutions were made up on the basis of gram equivalents of anhydrous salt per one thousand grams of water. The solutions used were barium chloride at concentrations of 3.2, 2.8 and 1.6 weight normal, and the mixed salt $\text{NaCl} : 1/2\text{BaCl}_2$ at concentrations of 3.2, 1.6, 0.8 and 0.4 weight normal. The mixed solution was prepared by diluting a volume of the solution of one of the salts with an equal volume of the solution of the same concentration of the other salt. Thus one volume of 0.8 wt.N. NaCl and one volume of 0.8 wt.N. BaCl_2 were mixed and called 0.8 wt.N. of the mixed salt.

The value of the reversible molal heat of dilution was obtained by diluting the solution at a definite concentration with decreasing amounts of water, and plotting the heat effect obtained against the number of mols of water added. The curve was found to be a straight line at this region so that, by extrapolation to zero mols of water added, the value of the reversible molal heat of dilution at any concentration could be obtained. That is, this value would approximate the quantity of heat absorbed or evolved when one mol of solvent is added to an infinite quantity of solution.

ACCURACY. The very small values of the heat effects in the case of the more dilute solutions necessitated only approximate results here. MacInnes and Braham state that heat effects of from 50 to 60 calories can be measured with an accuracy of from four to five per cent. With a total heat effect of from 5 to 20 calories one should not expect much more than 30 to 50 per cent accuracy. In these cases, however, an error of even 100 per cent would change the point on the curve of the concentration plotted against the molal heat effect to such a slight extent that the curve itself would be unaffected. In the case of the larger heat effects, running as high as several hundred calories, the heat change can be measured to within a fraction of one per cent, so that the error of the reversible heat value should not exceed one to two per cent.

EXPERIMENTAL DATA.

Tables I to VII give the heats of dilution of the various solutions studied, together with the data from which these are obtained. In these tables, 'Time' is the time in seconds during which electrical energy was passed through the calorimeter heater; 'Res.' is the reading of the resistance in ohms of the platinum resistance thermometer; ' $\Delta R \times 10^5$ ' is the change of resistance of the thermometer in ohms multiplied by 10^5 ; 'Gm. Sol.' is the amount of solution placed in the calorimeter; 'Mols H_2O ' is the number of mols of water used for the dilution; 'Amp.' is the current in amperes passed through the calorimeter heater; 'E.M.F.' is the voltage drop across the leads of the calorimeter heater; 'Cal.' is the amount of electrical energy in calories passed through the heater; 'Total Heat Effect' is the heat effect due to the dilution; this value divided by the number of mols of water added gives the 'Heat Effect per Mol'.

SAMPLE CALCULATION. Data taken from table II, first dilution. If 502 calories produce a change of resistance of 507 units, then a change of resistance of 37 units in the same amount of the same solution in the same apparatus would be produced by 26.75 calories. This is the heat of dilution due to 35 mols of water. The heat effect per mol is therefore 26.75 divided by 35 or 0.77 calories. In this case, since the resistance actually decreased, the sign would be negative.

Table I - Heat of Dilution of 3.2 wt.N. BaCl₂.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol
	27.31500		10,000	35					
	0981	-96							
180	0885	645			2.374	6.79	694.		
-	1530	-	-	-	-	-	-	-102.	-2.9
-	27.32500	-	-	-	-	-	-	-	-
	1879	-94	10,000	35					
270	1785	1026			2.365	6.80	1035.		
-	2811	-	-	-	-	-	-	-95.	-2.7
-	27.43500	-	-	-	-	-	-	-	-
	0916	-41	10,000	25					
390	0875	1680			2.45	6.90	1575		
-	2555	-	-	-	-	-	-	-43.7	-1.8
-	-	-	-	-	-	-	-	-	-

These results are not to be relied on to any great extent due to the fact that at this concentration the solution is almost at its saturation point. The most probable indication of the value of the reversible molal heat of dilution is the first or second dilution, giving a value of between 2.9 and 3.0 calories per mol.

Table II - Heat of dilution of 2.8 wt.N. BaCl₂

Time	Res.	AR x 10 ⁵	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.31500		10,000	35					
	4880	-37							
	4843	507			2.47	7.08	502.		
120	5350	-	-	-	-	-	-	-26.75	-0.77
	27.55500		10,000	25					
	0263	-21							
	0242	3045			3.49	10.20	3147		
370	3287	-	-	-	-	-	-	-22.0	-0.88
	27.53500		10,000	15					
	2134	-16							
	2118	1015			3.24	9.30	973		
135	3133	-	-	-	-	-	-	-15.3	-1.02
									-1.20 cal/mol.

Reversible Molal Heat of Dilution, L_D

Table IV - Heat of Dilution of 3.2 wt.N. NaCl:1/2BaCl₂

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.46500								
	3713	-250	10,000	35					
	3463								
120	3874	411			2.345	6.74	454	-276.5	-7.89
-	-	-	-	-	-	-	-	-	-
	27.46500								
	0300		10,000	25					
	27.45500	-210							
	1090								
240	1760	670			2.385	6.82	930	-232.	-9.3
-	-	-	-	-	-	-	-	-	-
	27.43500								
	2105	-185	10,000	15					
	1920								
120	2420	500			2.385	6.80	465	-172.2	-11.48
-	-	-	-	-	-	-	-	-	-
Reversible Molal Heat of Dilution, L _D (Observed)									-14.1 cal./mol.
(Calculated)									-10.25 cal./mol.

Table V - Heat of Dilution of 1.6 wt.N. NaCl:1/2BaCl₂

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.49500								
	3485	-142	10,000	35					
	3343								
120	4008	665			2.30	6.55	646.	-138.	-3.94
-	-	-	-	-	-	-	-	-	-
	27.49500								
	3115	-108	10,000	25					
	3007								
180	3667	660			2.30	6.56	649.	-106.2	-4.25
-	-	-	-	-	-	-	-	-	-
	27.49500								
	3890	-65	10,000	15					
	3825								
120	4250	425			2.30	6.58	434.	-66.4	-4.50
-	-	-	-	-	-	-	-	-	-
Reversible Molal Heat of Dilution, L_D (Observed)									
								-4.93 cal./mol.	
								(Calculated)	
								-3.98 cal./mol.	

Table VI - Heat of Dilution of 0.8 wt. N. NaCl:1/2BaCl₂

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.57500								
	5010	-59	10,000	35					
	4951				2.15	6.21	382.5		
120	5360	409						-55.2	-1.57
-	-	-	-	-	-	-	-	-	-
	27.29500								
	4052	-40	10,000	25					
	4012								
120	4385	373			2.18	6.24	380.	-40.7	-1.63
-	-	-	-	-	-	-	-	-	-
	27.30500								
	4709	-26	10,000	15					
	4683								
120	5085	402			2.11	6.07	370.	-25.42	-1.69
-	-	-	-	-	-	-	-	-	-
Reversible Molal Heat of Dilution, L _D (Observed)									
								-1.78 cal/mol.	
							(Calculated)	-1.50 cal/mol.	

Table VII - Heat of Dilution of 0.4 wt.N. NaCl:1/2BaCl₂

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H ₂ O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.34500		10,000	40					
	2121	-9							
	2112								
210	2580	468			2.17	6.26	680	-12.05	-0.30
-	-	-	-	-	-	-	-	-	-
	27.51500		10,000	35					
	2996	-13							
	2983								
180	3638	645			2.32	6.62	663	-13.35	-0.38
-	-	-	-	-	-	-	-	-	-
	27.51500		10,000	25					
	3040	-13							
	3027								
120	3460	433			2.33	6.65	444.5	-12.6	-0.50
-	-	-	-	-	-	-	-	-	-
Reversible Molal Heat of Dilution, L_D (Observed)									-0.75 cal./mol.
(Calculated)									-0.78 cal./mol.

DISCUSSION

Figures VI to XIV give the graphical representation of the results of the heats of dilution as given in the tables. Mols of water of dilution are abscissae and molal heat effects in calories are ordinates.

Figures VI and VII give the molal heat effect of a barium chloride solution of a certain concentration as a function of the number of mols of water added; while Figure VIII gives the change of the reversible molal heat of dilution with the concentration of the barium chloride solutions. Figure IX is the curve for the heats of dilution of solutions of sodium chloride at various concentrations. The data for this curve is taken from the Doctor's Dissertation of A. E. Stearn.

Figures X to XIII are the curves for solutions of the mixed salt $\text{NaCl}:\frac{1}{2}\text{BaCl}_2$ which are analogous to VI and VII for BaCl_2 , while the curve in Figure XIV marked "Obs" is the curve for this mixed salt analogous to Figure VIII for barium chloride. The other curve in this Figure marked "Calc." is the curve obtained from the sum of the heats of dilution of the separate constituents of the mixture at their respective concentrations.

It is seen that with increasing concentration these two curves in Figure XIV diverge more and more. This seems explicable only on the assumption that with increasing concentration there is an increasing tendency to form higher order complexes between the salt constituents due to their mass action. Thus, at low concentrations, where these complexes would

be present only in small amounts their specific effect should be negligible, and the two curves should tend to coincide. This is seen actually to be the case.

The behavior of the barium chloride solutions and the solutions of the mixed salt as found in this investigation is very similar to that of solutions of strontium chloride and of mixed salts of strontium chloride with the alkali chlorides.

Fig VI
2.8 N BaCl₂.

-1.2
-1.1
-1
-.9
-.8
-.7 0

5

10

15

20

25

30

35

25

40

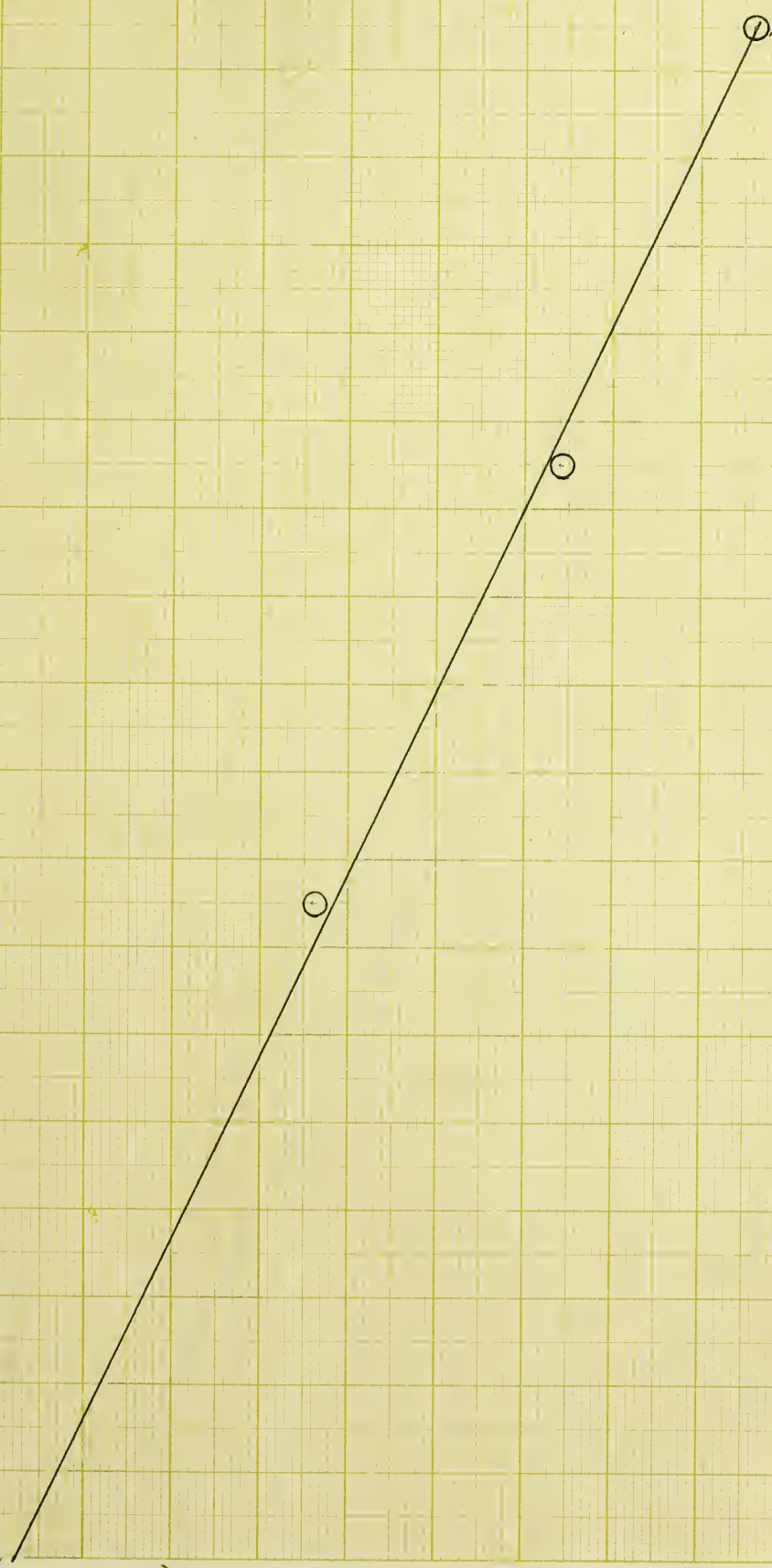


Fig VII.
1.6 N Ba Cl₂.

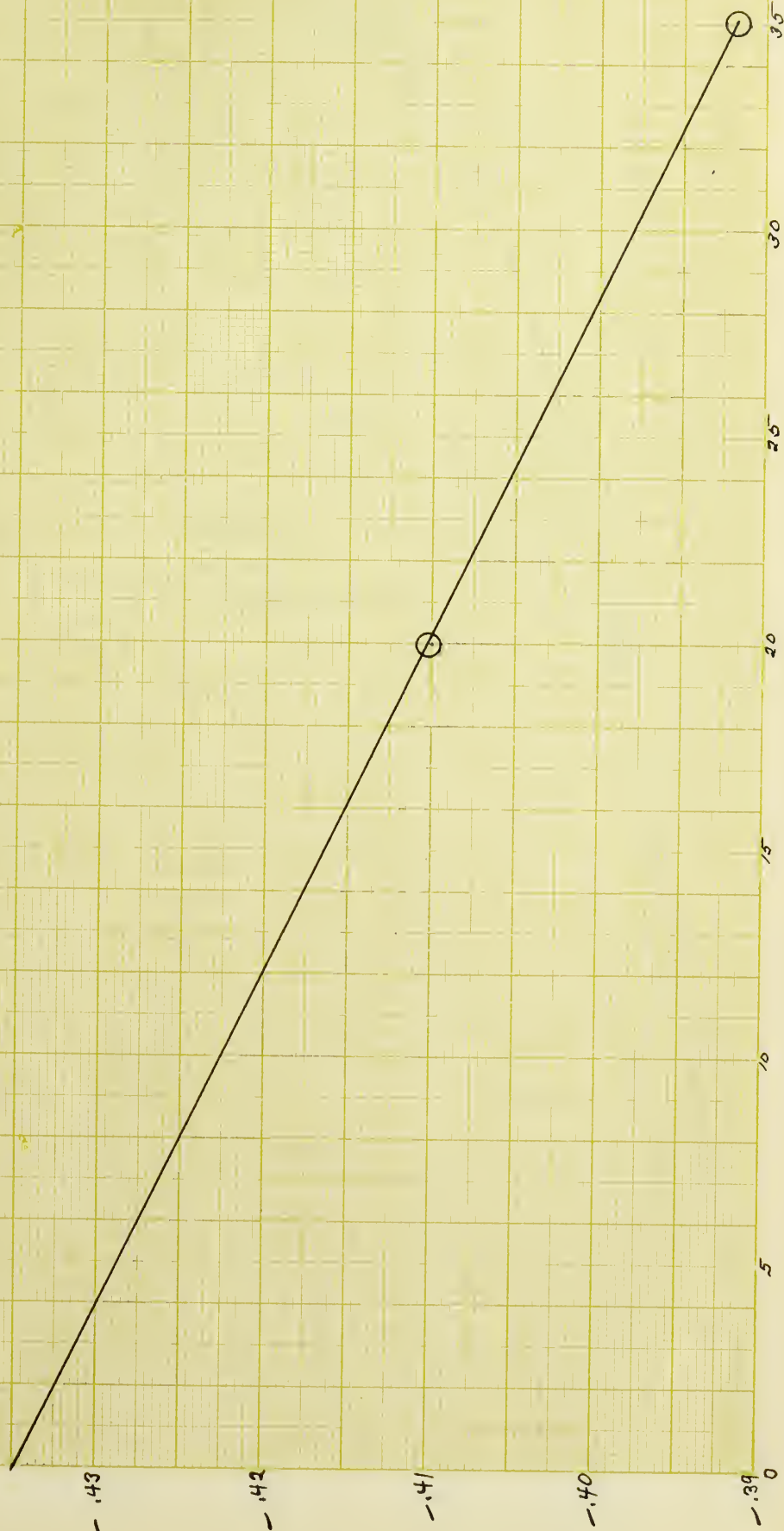


Fig VIII

BaCl₂

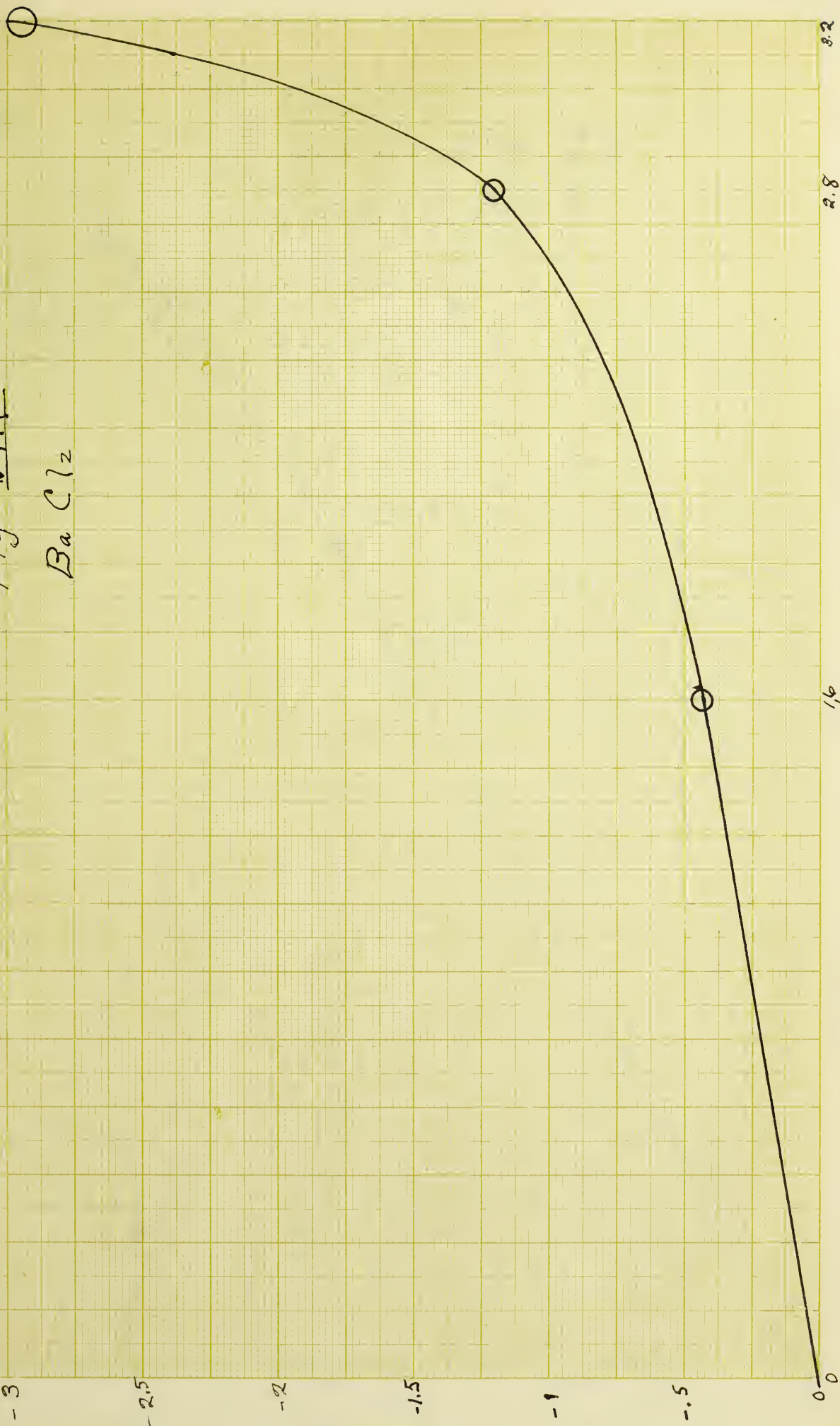


Fig IX
NaCl

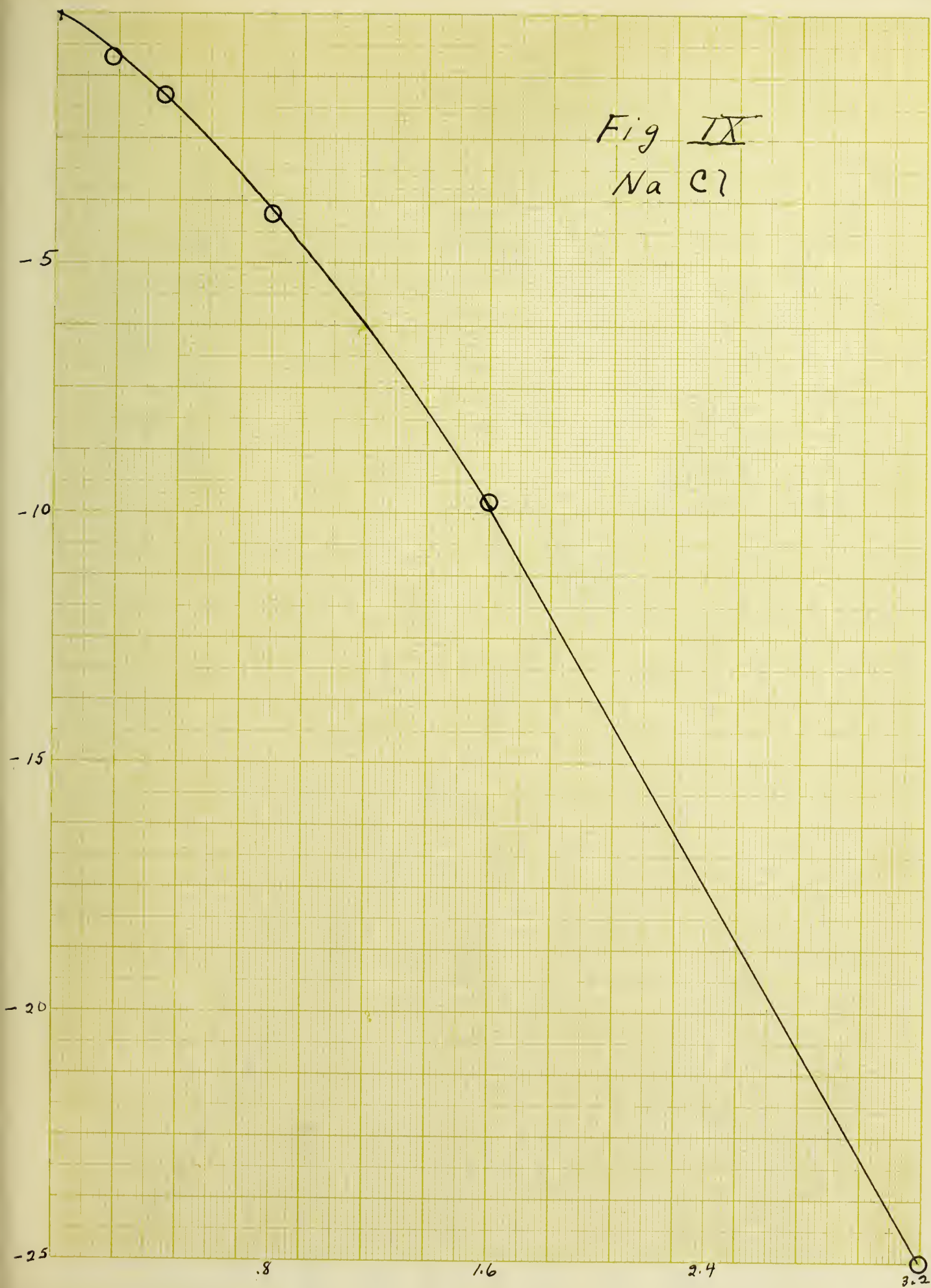


Fig X
3.2N NaCl · $\frac{1}{2}$ BaCl₂

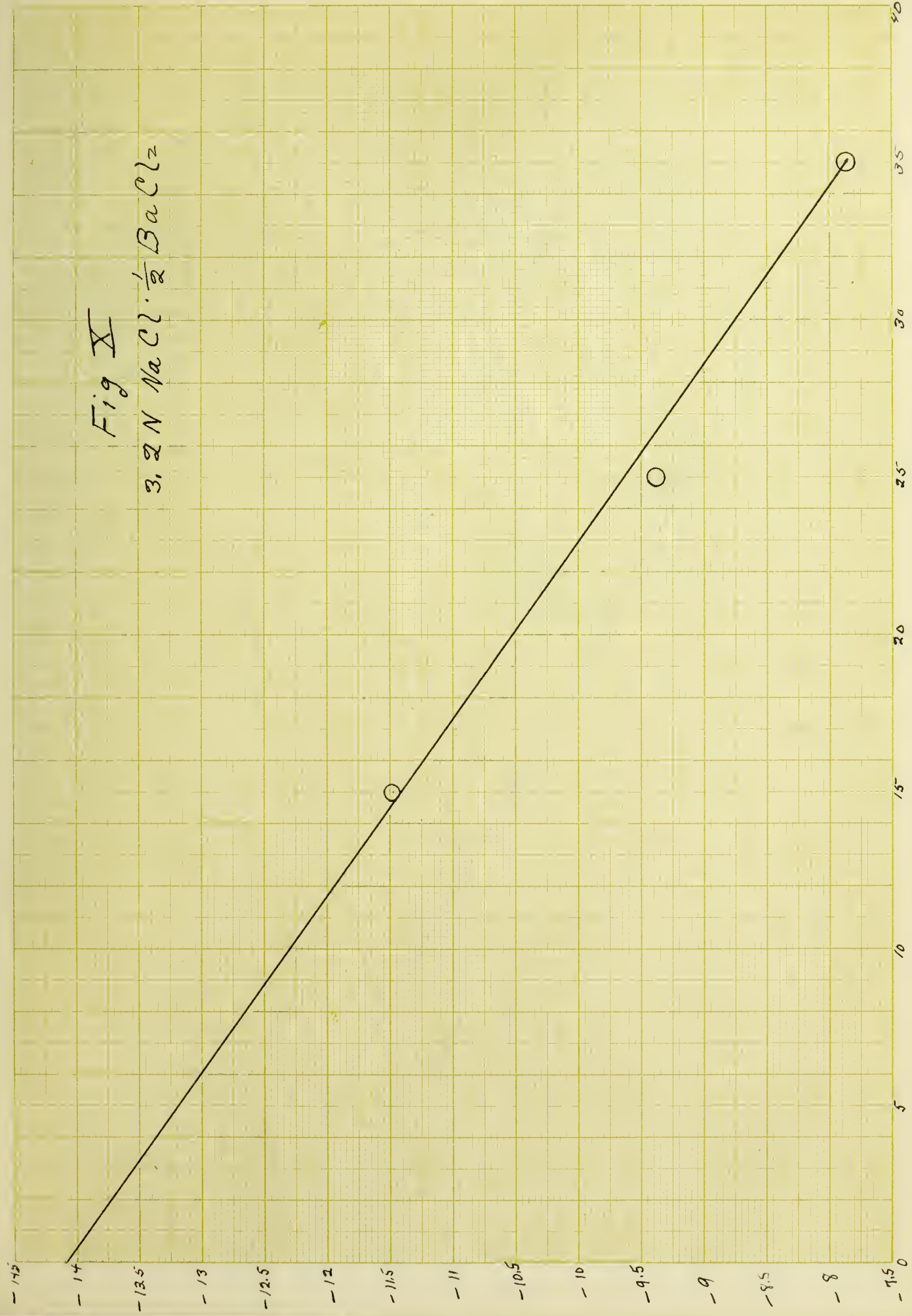


Fig XI.

1.6 N $\text{NaCl} \cdot \frac{1}{2} \text{BaCl}_2$.

-5
-4.9
-4.8
-4.7
-4.6
-4.5
-4.4
-4.3
-4.2
-4.1
-4
-3.9 0

5

10

15

20

25

30

35

40

30

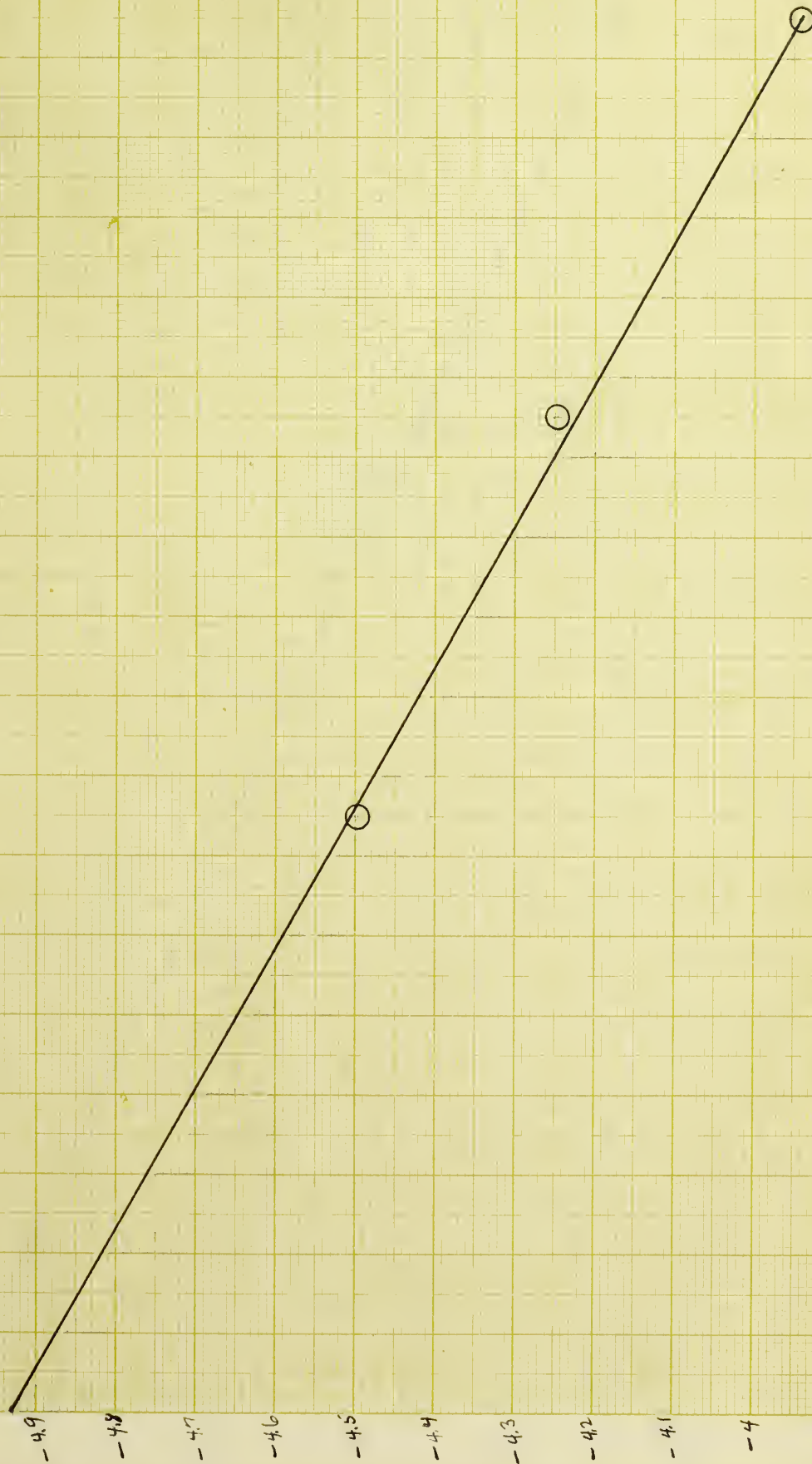


Fig XIII
.8N NaCl · $\frac{1}{2}$ BaCl₂.

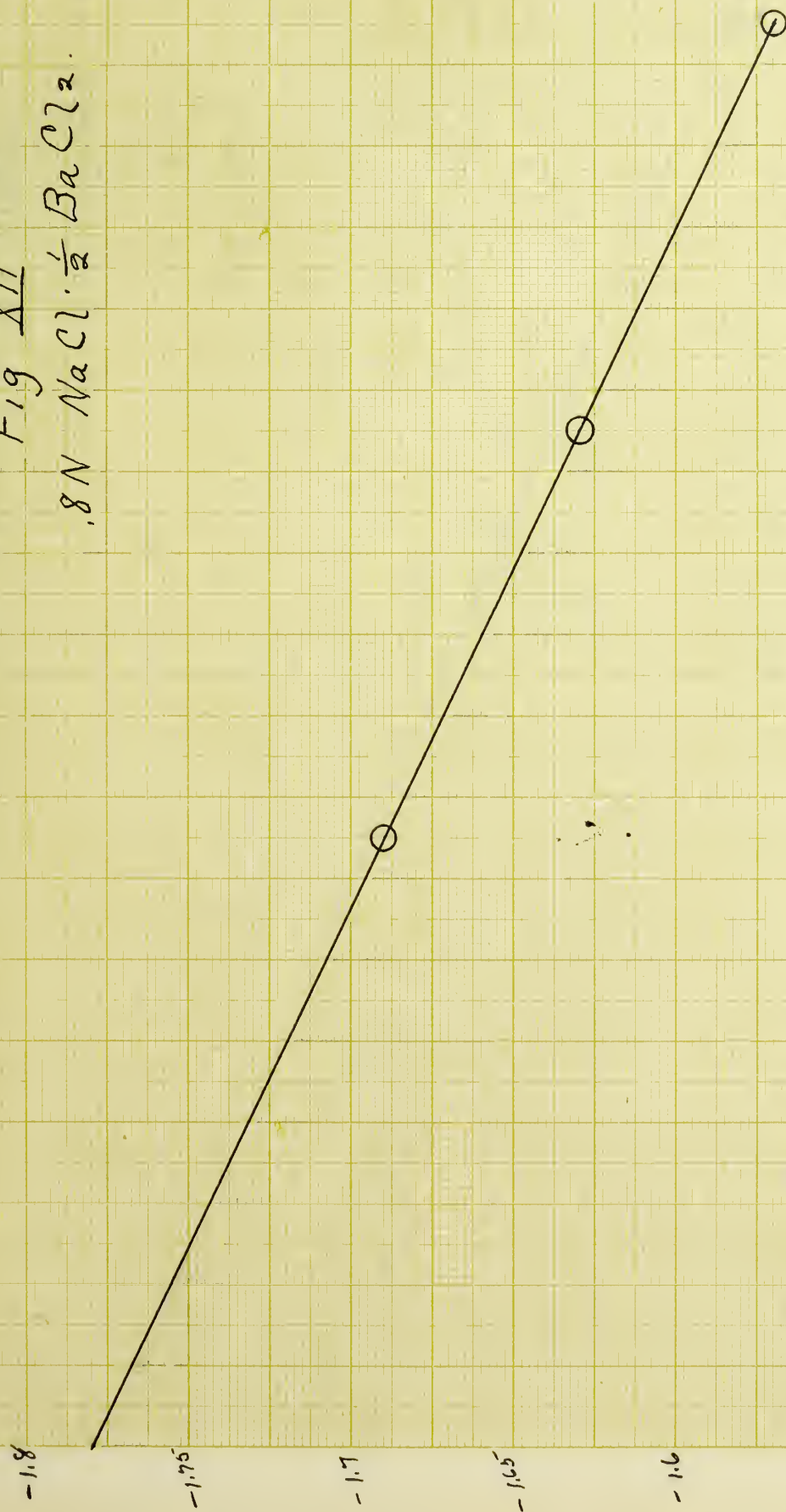


Fig XIII

.4 N $\text{NaCl} \cdot \frac{1}{2} \text{BaCl}_2$

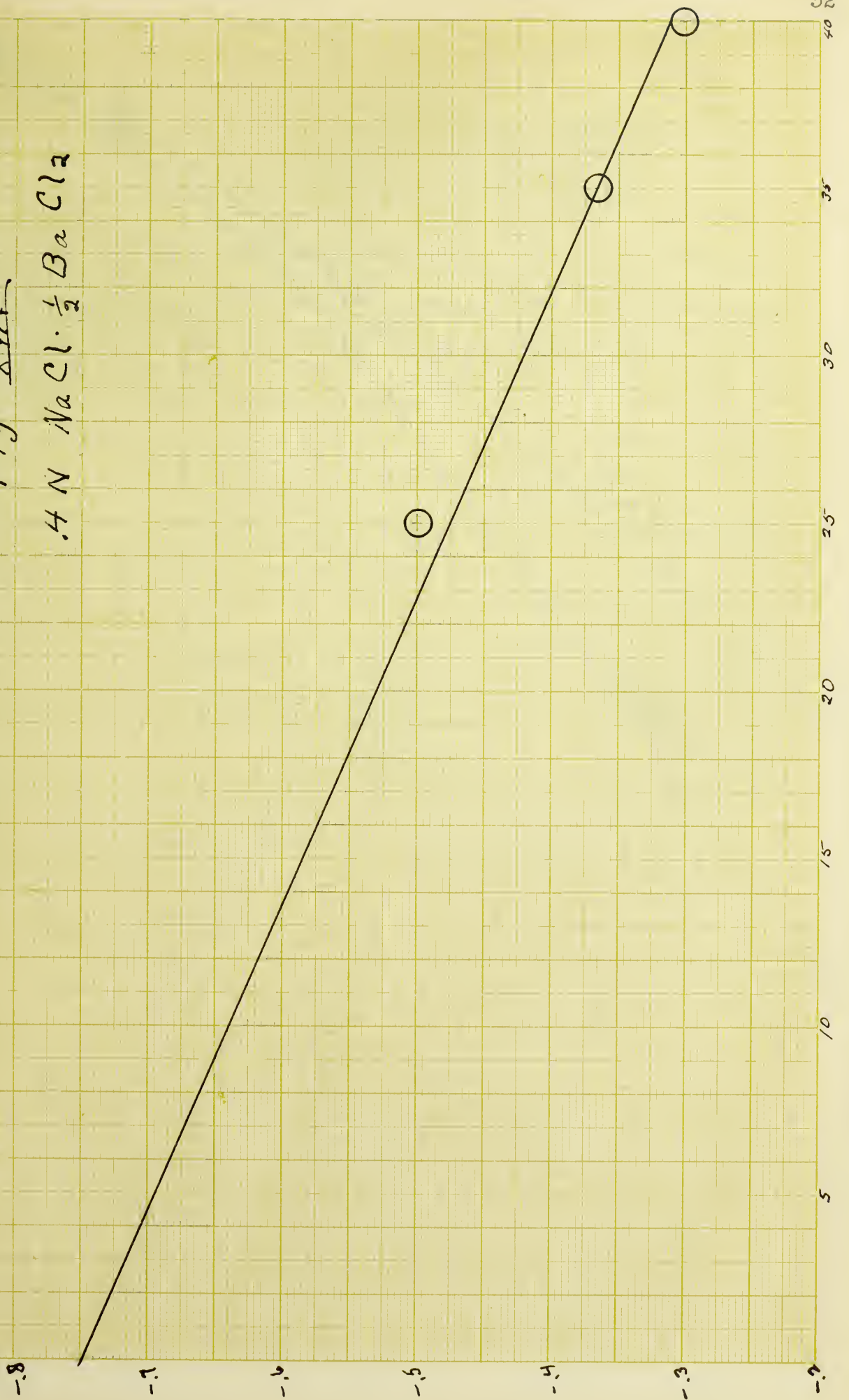
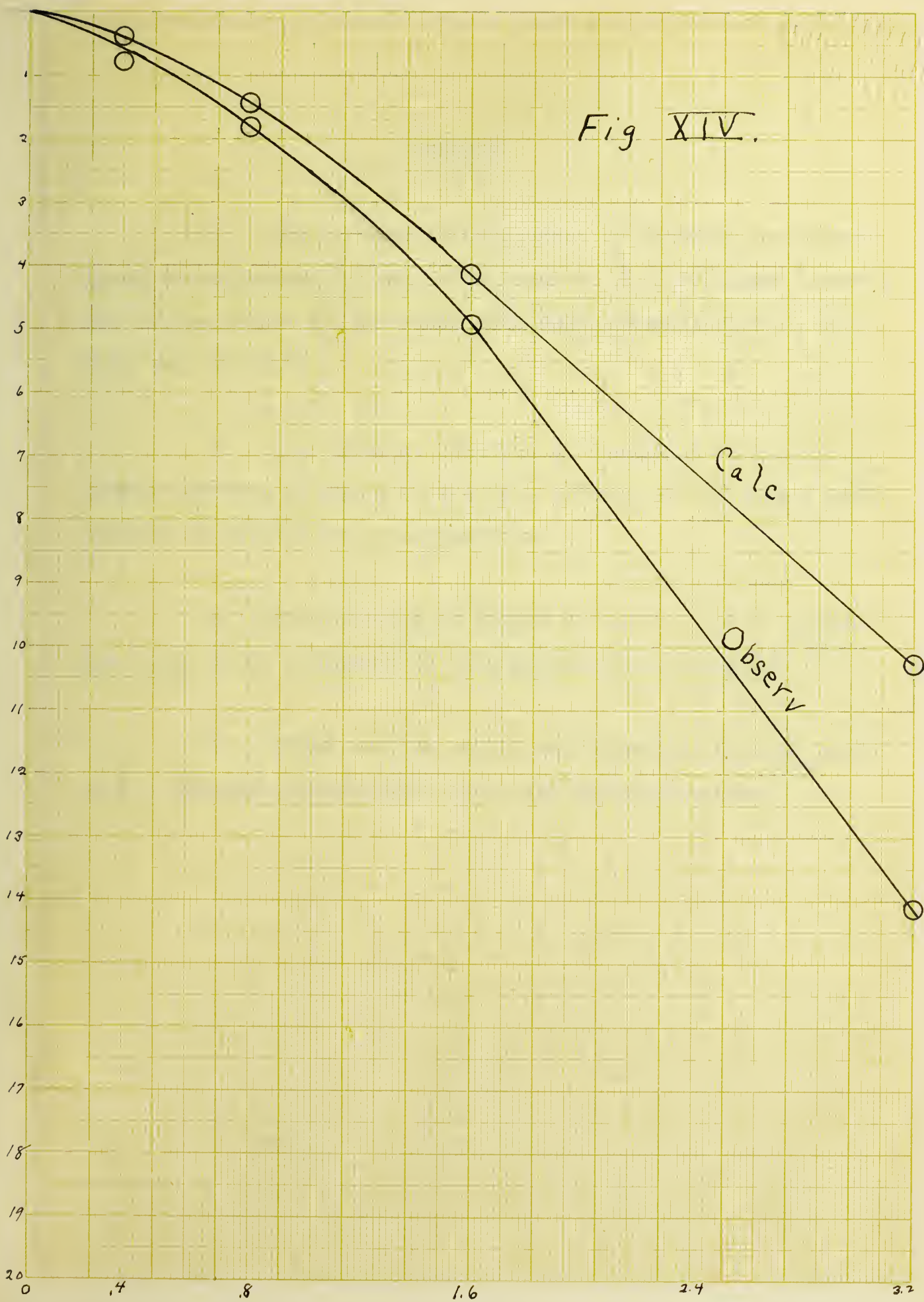


Fig XIV.



SUMMARY

1. The reversible molal heat of dilution was determined for solutions of barium chloride of 3.2, 2.8, and 1.6 wt.N and for solutions of the mixed salt $\text{NaCl}:\frac{1}{2}\text{BaCl}_2$ at 3.2, 1.6, 0.8, and 0.4 wt.N.

2. The heats of dilution of the mixed salt bore no simple additive relation to the heat effects of the simple components at equivalent concentrations.

3. The behavior of barium chloride in this respect was found to be analogous to that of strontium chloride.⁽¹⁾

4. These results can be explained on the same basis as the results obtained with the mixed strontium salts.⁽¹⁾

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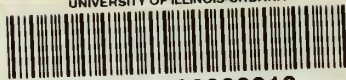
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